

SYNTHESIS AND NMR CHARACTERIZATION OF ALIPHATIC-AROMATIC COPOLYESTERS BY REACTION OF POLY(ETHYLENE TEREPHTHALATE) POST-CONSUMER AND POLY(ETHYLENE ADIPATE)

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An aliphatic-aromatic copolyester of poly(ethylene terephthalate), PET, and poly(ethylene adipate), PEA, PET-co-PEA, was synthesized by the high temperature melt reaction of post-consumer PET and PEA. As observed by NMR spectroscopy, the reaction yielded random copolyesters in a few minutes through ester-interchange reactions, even without added catalyst. The copolyesters obtained in the presence of a catalyst presented higher intrinsic viscosity than that obtained without the addition of catalyst, due to simultaneous polycondensation and ester-interchange reactions. The structure of the aliphatic-aromatic copolyesters obtained in different PET/PEA ratio is random as observed by NMR analysis.

Keywords: aliphatic-aromatic copolyesters; polyethylene terephthalate; chemical recycling.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a polyester widely used in many everyday applications, mainly due to its low production cost, good mechanical properties and recyclability. PET is commonly encountered in plastic bottles for soft drink and in films which are used for food and liquid packaging, magnetic tapes and novelty balloons, among others applications^{1,2}. PET is a non-biodegradable polymer, resistant to hydrolysis in mild pH conditions, innocuous to human body, it is looked as a noxious material due to the great volume in waste streams and high resistance to atmospheric and biological agents^{2,3}.

One possible solution for this problem would be the development of new biodegradable polymers. The commercially available biodegradable polymers are mostly aliphatic polyester, as for example, poly(3-hydroxyalkanoate)s, poly(ϵ -caprolactone) and so on, this polyesters including their copolyester can cover a wide range of properties needed for most purposes⁴. The development of new types of biodegradable polymers with different properties of conventional aliphatic polyesters is highly desirable due to the great number of specific requirements for polymeric materials⁴.

In this way, the modification of non-biodegradable polymers with biodegradable polymers, for example, incorporating aliphatic units in the PET chain either by polymer-polymer transesterification or by copolymerization of the commonomers², resulting in aliphatic/aromatic copolyester is an interesting way to develop new biodegradable copolymers. The reactive blending of the well known homopolyesters is an inexpensive method to obtain new aliphatic/aromatic copolyesters with intermediates properties⁵.

The modification of PET structure with 10% of poly(ethylene adipate) PEA make it biodegradable in typical environmental conditions in the presence of water⁶. The hydrolysable poly(ethylene terephthalate-co ethylene adipate) shows a loss of weight for samples exposed to PH 7,0 water at 80 °C, whereas no change was

observed at room temperature. The copolyester was synthesized by simple ester exchange in the melt state of PET and PEA, stannous octoate was used for catalyzing the reaction which was performed at 265 °C for 3 h under vacuum⁶.

Copolyesters composed of aliphatic and aromatic units, such as, 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, sebacic acid, adipic acid and terephthalic acid combined in an appropriate ratio has proved to be biodegradable^{7,8}.

The biodegradation behavior of copolyesters which contains aliphatic and aromatic subunits are dependent on composition, length and sequence distributions of aliphatic and aromatic units, cristalinity and melting temperature^{9,10}.

It was shown that the biodegradability of chain segments consisting only of aromatic dicarboxylic acids, is particularly dependent on the number of repeating units^{8,9}. It is necessary to know the degree of randomness of the copolyesters chains and the block length distribution to understand the biodegradation behavior of aliphatic/aromatic copolyesters¹⁰.

With the NMR spectroscopy the study of the molar fraction of the acids, the degree of randomness among other informations may be known. These data are very important to the understanding of the biodegradability properties of the aliphatic/aromatic copolyesters.

Recycling post-consumer PET into aliphatic-aromatic copolyesters exhibiting enhanced biodegradability, together with fair mechanical properties, is a potentially interesting approach: The use of ecofriendly, compostable plastics obtained from PET would be an elegant way of dealing with the problem of PET waste disposal.

In this work, we discuss the synthesis and characterization by NMR of aliphatic-aromatic copolyesters obtained by the high temperature melt reaction of post-consumer poly(ethylene terephthalate) PET with poly(ethylene adipate) PEA forming a copolyester PET-co-PEA, showing that it is possible to transform the post-consumer PET in another material by simple interchange ester-ester reaction.

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EXPERIMENTAL PART

Materials and methods

The catalyst utilized in all polymerization reactions was (Titanium butoxyde (IV)), obtained from Aldrich and used without further purification. Ethylene glycol from Merck and adipic acid from Vetec were used as received.

Synthesis of Poly(ethylene adipate)- (PEA)

PEA was prepared according the procedures described in the literature¹¹. That is, by polycondensation reaction between the monomers ethylene glycol (EG) and adipic acid (AA) with an initial proportion of (EG/AA=3/1), with elimination of water and EG. $[\eta] = 0.0104 \text{ mL/mg}$

Synthesis of copolyesters PET/PEA

Samples of PET post-consumer ($[\eta] = 0.0736 \text{ mL/mg}$, $X_c = 31\%$) were cuted and dried at 100°C for 1 h prior to use.

The copolymerization reactions were carried out in a 500 mL reactor system equipped with an air-driven stirrer, a thermocouple, a nitrogen inlet tube and vacuum system. The reactor is heated by means of an electrical mantle. The temperature is monitored via an Pt 100 thermocouple with a temperature controller. The mantle is connected to the automatic controller. The copolymers PET and PEA were synthesized in different ratios. In a typical reaction, PEA and PET (total weight 100g) are added, under N_2 , to the reactor and heated in approximately 15 min until 240°C , then the catalyst (0.146 mmol) (in the reactions with added catalyst) is added into the reaction flask. Then vacuum (0.040 mmHg) is applied (at this step we start to count the reaction time), and the reaction is maintained for the desired reaction time. Then the reaction is stopped and the copolymer was put in another vessel at room temperature.

NMR analysis

Proton NMR spectra, of resultant copolyesters, were recorded on a Bruker - 300 MHz spectrometer, chloroform + trifluoroacetic acid (3/1 mL/mL) solution was used as the solvent. Chemical shifts were reported relative to the residual protons of chloroform-d (7.26 ppm). The NMR spectra were treated using MestRe-C 2.1.1 (Magnetic Resonance Companion, NMR Data Processing Program)

Viscosity measurements

The intrinsic viscosities $[\eta]$ of the copolymers were measured in chloroform solutions with an Ubbelohde viscometer thermostated at $25^\circ\text{C} \pm 0.05^\circ\text{C}$. The intrinsic viscosity of the PET sample was measured in dichloromethane + trichloroacetic acid (4/1 g/g) solution in the same viscometer thermostated at $25^\circ\text{C} \pm 0.05^\circ\text{C}$.

RESULTS AND DISCUSSION

Aliphatic-aromatic copolyesters are formed by the high temperature melt reaction of post-consumer PET with poly(ethylene adipate) (PEA), even without added catalyst. The copolymers obtained can presents three different sequences structures represented by TET (terephthalate, ethylene, terephthalate), AEA (adipate, ethylene, adipate) and TEA (terephthalate, ethylene, adipate) in Figure 1.

The NMR analysis allowed us to observe the copolymer formation, the $^1\text{H-NMR}$ spectra for PET, PEA and for a copolyester PET-co-PEA (50/50, wt%) are shown in Figure 2 and the chemical shift and assignment of proton signal showed in $^1\text{H NMR}$ spectra are listed in Table 1.

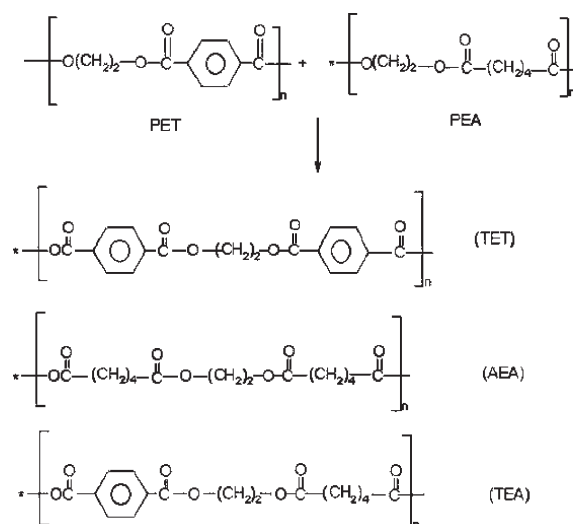


Figure 1. Possible sequences structures for the obtained copolyester

Table 1. Chemical shift and assignment of proton signal showed in $^1\text{H NMR}$

Structural Unit	Chemical Shift (ppm)
$-\text{OOC}-\overset{\text{b}}{\text{CH}_2}-\overset{\text{a}}{(\text{CH}_2)_2}-\overset{\text{b}}{\text{CH}_2}-\text{COO}-$	a 1.67 b 2.35
A - $\overset{\text{c}}{\text{CH}_2}\text{CH}_2 - \text{OH}$	c 3.82
T - $\overset{\text{d}}{\text{CH}_2}\text{CH}_2 - \text{OH}$	d 3.97
A - $\overset{\text{e}}{\text{CH}_2}\text{CH}_2 - \text{A}$	e 4.22
T - $\overset{\text{g}}{\text{CH}_2}\text{CH}_2 - \text{A}$	f 4.42 g 4.52
T - $\overset{\text{h}}{\text{CH}_2}\text{CH}_2 - \text{T}$	h 4.69
$\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}$	i 8.1

As we can see from Figure 2 and Table 1 spectra (a) show the typical peaks of PET, the peak centered in 8.16 ppm can be assigned to benzene ring and the peak at 4.82 ppm to the ethylenedioxy group of PET. In the spectra (b) of PEA, we can see the peaks in 1.66 ppm that belongs to $-(\text{CH}_2)_2-$, and another peak in 2.35 ppm that can be assigned to $-\text{CH}_2\text{COO}-$ in PEA units, in 4.26 ppm we observe the ethylenedioxy group of PEA. In the NMR spectra (c) of PET-co-PEA, except for the nuclear resonance characteristic of PET and PEA, we can see new peaks appearing in the range of 4-4.8 ppm. We attribute these peaks to the formation of new bonds for the sequences structures TEA showed in Figure 1. In 4.22 ppm the peak is attributed to methylene protons of the ethylenedioxy group in ET unit linking an adipate unit in AEA segment. The peak at 4.42 ppm is the contribution of methylene protons of the ethylenedioxy group in ET unit linking an adipate unit in TEA segment. The signal at 4.52 ppm is assigned to methylene protons of the ET group in the TEA segments next to a terephthaloyl group.

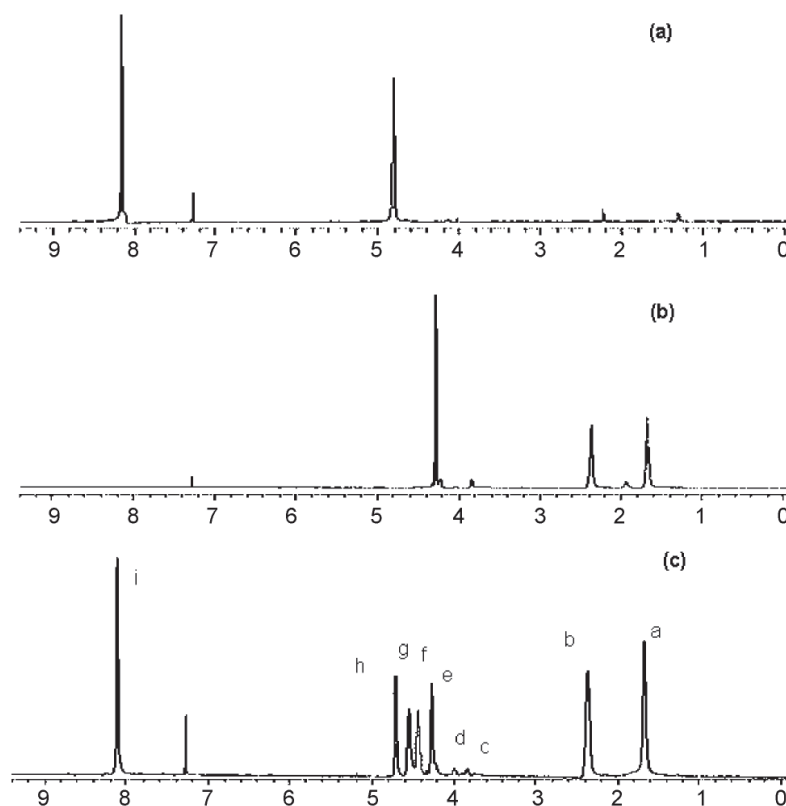


Figure 2. NMR spectra (a) PET, (b) PEA and (c) PET-co-PEA (50/50% wt)

Finally, the peak at 4.69 ppm is attributed to methylene units of TET segments. These attributions are in agreement with that for a copolymer PET-co-PEA (90/10)⁶. We can also observe two signals one in 3.82 and another in 3.97 which are attributed to the resonances of the ethylene glycol group at the end of the chain as depicted from Figure 2 and Table 1.

In order to observe the evolution of copolymer formation with time and the behavior of intrinsic viscosity, we obtained samples of PET-co-PEA (50/50% wt) at different reaction times (time in which the mixture was under vacuum), 0, 1, 3, 5, 10, 20, 40, 60 and 120 min. The samples PET-co-PEA were obtained from the homopolymers PEA ($[\eta]$ = 0.0104 mL/mg) and PET post-consumer ($[\eta]$ = 0.0736 mL/mg) in the conditions described in experimental section. The intrinsic viscosity of the copolymers was estimated and increases with reaction time until 20 min, after that time we observe the degradation of copolymer assigned by both decrease in viscosity and the appearing of new peaks in the NMR spectra. Copolyesters PET-co-PEA obtained with addition of a catalyst during the synthesis resulted in a copolymer with higher viscosity than those obtained in the same reactions conditions but without the addition of catalyst. This behavior is due to simultaneous polycondensation and ester-interchange reactions in synthesis with the addition of a catalyst, instead in these reactions without addition of a catalyst we have only ester-interchange reactions. Table 2 summarizes the behavior of intrinsic viscosity with the reaction time and the influence of catalyst addition. For copolyester synthesis in times of 1 and 3 min we observed the signals in NMR spectra attributed to TEA segments formation of copolyester but the intrinsic viscosity obtained were very low.

As we can see from Table 2 the lowest values for intrinsic viscosity were obtained for the reaction without catalyst added and varied from 0.0101 mL/mg (entry 1) for 5 min of reaction time to 0.0116 mL/mg (entry 3) for 20 min of reaction time. For reactions

Table 2. Variation of the intrinsic viscosity $[\eta]$ of PET-co-PEA (50/50% wt) with reaction time for reactions with and without catalyst added

Entry	Reaction time min	$[\eta]$ - With catalyst added*# mL/mg	$[\eta]$ - Without catalyst added# mL/mg
1	5	0.0108	0.0101
2	10	0.0117	0.0109
3	20	0.0152	0.0116
4	40	0.0132	–
5	60	0.0133	–

*Titanium butoxyde (IV); #245 °C under vacuum at desired time

with catalyst added we observe the same behavior, which means, the intrinsic viscosity increases with reaction time, the lowest obtained value is 0.0108 mL/mg (entry 1) for 5 min of reaction time and the highest is 0.0152 for 20 min of reaction. For samples with catalyst addition, which had their viscosity evaluated, for reaction time equal or superior to 40 min we observed the polymer degradation and a decrease in intrinsic viscosity.

In utilizing the best reaction time, 20 min, for samples PET-co-PEA (50/50, wt%) we synthesized copolyesters with different ratio of PET/PEA with addition of catalyst in order to see the behavior of intrinsic viscosity and the polymer structure. The evaluation of intrinsic viscosity for samples with more than 50% in weight of PET content was difficult due to their partial solubilization in CHCl_3 , so for these compositions we will only presents the study by NMR of polymer structure that will be discussed later.

We have a strict relationship between biodegradability and terephthalic acid content. Biodegradability decreases with increase of PET content^{7,8,10}. So, varying the terephthalic acid content, we are

Table 3. Calculated molar ratio values from NMR spectra to samples (50,50 wt%) PET-co-PEA

Entry	Reaction time (min)	TET segment		AEA segment		TEA segment	
		With cat.	Without cat.	With cat.	Without cat.	With cat.	Without cat.
1	5	0.201	0.200	0.299	0.219	0.499	0.501
2	10	0.192	0.195	0.313	0.321	0.494	0.482
3	20	0.218	0.193	0.264	0.323	0.517	0.481
4	40	0.219	–	0.253	–	0.526	–
5	60	0.210	0.210	0.285	0.274	0.504	0.512

Table 4. Calculated molar ratio values from NMR spectra to samples with different PET/PEA ratios

Entry	PET/PEA wt, % ratio	Calculated value TET/AEA/TEA	Calculated value from NMR spectra TET/AEA/TEA
7	60/40	0.33/0.18/0.49	0.36/0.16/0.47
8	70/30	0.46/0.10/0.44	0.47/0.09/0.43
9	75/25	0.53/0.07/0.39	0.62/0.06/0.31
10	80/20	0.61/0.05/0.34	0.76/0.07/0.18

altering mechanics and the biodegradability properties of copolyester. These changes allow us to adapt the obtained copolyester to desired applications, finding a compromise between biodegradability and mechanical properties. The biodegradability and hydrolysis behavior of the samples PET-co-PEA are being evaluated.

From the NMR spectra we can calculate the average block length of aromatic and aliphatic units, if we have block copolyesters, and the randomness of the copolyester if we have synthesized random copolyester.

If we have random copolyesters, the experimental molar ratio must be equal to their probability of existence calculated by statistics, so, theoretically, for the reaction of 1 mol of PET and 1 mol of PEA, the probability that the segments TET, AEA and AET occur are 25, 25 and 50% respectively. If we had block copolyester the probability would be 0.5% to the TET segment and 0.5% to the AEA segment.

The molecular weight for the repetition units of PET and PEA are 192.17 and 172.17g/mol respectively. For example, a copolymer PET/PEA (50/50 wt,%) if we have a random copolymer, theoretically, the molar ratio of TET, AEA and AET occur are 0.25, 0.25 and 0.50 respectively. If we had block copolyester the probability would be 0.50 to the TET segment and 0.50 to the AEA segment.

Using the integral values from NMR spectra to calculate these relations we can see that we have random copolyester for all ratios PET/PEA and all reaction times. Table 3 shows the experimental molar ratio for PET-co-PEA (50/50 wt,%) calculated from integrals values from the NMR spectra for samples synthesized at different reaction time and with and without addition of a catalyst.

As we can see from Table 3 the experimental values calculated from NMR spectra allow us to state that even at reaction times of 5 min we have obtained a random copolyester in both cases, with and without catalyst addition (entry 1). For all reaction times we obtained experimental values near the theoretical values.

For the reactions with no additional catalyst added, it is important to emphasize, that we have an amount of residual catalyst from the copolymers PET and PEA, which must be active in the reaction of PEA and PET to form the copolymer.

Table 4 shows the calculated values for PET-co-PEA and those obtained experimentally through NMR spectra using the integral values to calculate the molar ratio for samples obtained at 20 min of reaction with catalyst addition and with different ratio of PET

and PEA. The same behavior is observed for all PET and PEA contents, showing that we have random copolyester in all cases.

It's important to note that in all reaction we utilized PET post-consumer, showing that is possible by chemical recycling to obtain a new copolymer and aiding to solve the problems in the waste stream. The NMR spectra obtained for samples synthesized at different times were quite similar, allowing us to conclude that the reaction occurred even before 5 min of reaction.

CONCLUSIONS

We showed in this work that we can obtain new copolymers PET-co-PEA from the reaction of PET post-consumer with PEA by high temperature molten reaction. The reaction of PET and PEA in different ratios and reaction time produces the formation of random copolymer even at times smaller of 5 minutes as we could see from NMR analysis.

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